Journal of Thermal Analysis and Calorimetry, Vol. 61 (2000) 107–117

X-RAY, THERMAL AND INFRARED SPECTROSCOPIC STUDIES ON POTASSIUM, RUBIDIUM AND CAESIUM URANYL OXALATE HYDRATES

N. D. Dahale, K. L. Chawla and V. Venugopal

Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India

(Received December 17, 1998; in revised form July 5, 1999)

Abstract

$M_2UO_2(C_2O_4)_2 \cdot nH_2O$ compounds (M=K, Rb and Cs) have been prepared and characterized by chemical and thermal analyses as well as by X-ray diffraction and infrared spectroscopy. X-ray powder data show that the compounds belong to an orthorhombic system. Thermal and infrared studies show that the compounds decompose to M_2UO_4 through the formation of alkali metal carbonate and UO_2 as intermediates. $K_2UO_2(C_2O_4)_2 \cdot 3H_2O$, and $Rb_2UO_2(C_2O_4)_2 \cdot 2H_2O$ gave K_2UO_4, Rb_2UO_4 at 700 and 600°C respectively, while in the case of $Cs_2UO_2(C_2O_4)_2 \cdot 2H_2O$, the intermediate products of decomposition reacted to yield $Cs_2U_4O_{13}$ at 1000°C.

Keywords: caesium uranyl oxalate, decomposition, DTA, potassium uranyl oxalate, rubidium uranyl oxalate, TG, X-ray diffraction

Introduction

The caesium–uranium–oxygen and rubidium–uranium–oxygen systems have been investigated extensively due to their chemical interactions in $(U,Pu)O_2$ fuels in fast reactors. Fission products caesium and rubidium have been observed to migrate radially and axially within the fuel pins. These elements can react with fuel forming corresponding uranates depending on oxygen potential and temperature. Cladding deformation and breach have been found and attributed to the formation of low density Cs–U–O and Rb–U–O compounds [1, 2]. Caesium and rubidium can react with oxide fuel forming hexavalent as well as lower valent uranates depending on the local oxygen pressure. The conflicting opinions center around the stability of the possible compounds, mainly Cs_2UO_4 and $Cs_2U_4O_{12}$ and conditions required for their formation. Systematic studies on the preparation, thermal stability, phase characterization and thermodynamic properties of such systems are being carried out at our laboratory.

Thermal decomposition of rubidium and caesium uranyl oxalate gave high purity phases of Rb_2UO_4, Cs_2UO_4, $Cs_2U_2O_7$, $Cs_4U_5O_{17}$ and $Cs_2U_4O_{13}$. The preparation of all the alkali metals and ammonium uranyl oxalates with UO_2^{2+} to $C_2O_4^{2-}$ ratio of 1:2 are reported

1418–2874/2000/ $ 5.00

[3]. X-ray structural analysis on $(NH_4)_2UO_2(C_2O_4)_2$ [4] and $K_2UO_2(C_2O_4)_2 \cdot 3H_2O$ [5] is available. In both the compounds the linear uranyl ion has five oxygen atoms forming a plane perpendicular to the O–U–O axis. The ammonium salt has the polymeric anion $[UO_2(C_2O_4)_2 \cdot H_2O]_n^{2n-}$ in which all the five oxygen atoms are from three oxalate groups, none of which are planar [4, 6]. The infrared spectrum of $K_2UO_2(C_2O_4)_2 \cdot 3H_2O$ has been discussed in terms of simple penta coordinated arrangement about the UO_2^{2+} ion, $K_2[UO_2(C_2O_4)_2 \cdot (H_2O)] \cdot 2H_2O$ involving two bidentate oxalate groups and one bonded water molecule [9]. This seems to be a substantially realistic approach and many of the hydrated salts have been written in this form, but no X-ray structural data are actually available to confirm it. The anhydrous compounds decompose when heated, forming metal uranates. The anhydrous potassium salt is reported to rehydrate stepwise to the monohydrate in air and to dihydrate, but not to the trihydrate on standing in a closed vessel over water for 12 h [3].

In previous studies X-ray and thermal analysis on $Li_2UO_2(C_2O_4)_2 \cdot 5H_2O$ and $Na_2UO_2(C_2O_4)_2 \cdot 4H_2O$ were reported [6]. The results of X-ray, thermal and infrared studies on $Rb_2UO_2(C_2O_4)_2 \cdot 2H_2O$ and $Cs_2UO_2(C_2O_4)_2 \cdot 2H_2O$ are discussed here. Potassium uranyl oxalate trihydrate has been prepared to compare its results with rubidium and caesium systems.

Experimental

Saturated solutions of rubidium or caesium oxalate and uranyl oxalate were mixed in equimolar proportions, heated to boiling and allowed to cool slowly. The yellow crystals separated were washed with ice cold water, alcohol and then dried in air. The method employed for the preparation of these compounds has been described earlier [3]. The X-ray diffraction (XRD) patterns were recorded on a Siemen's diffractometer using CuK_α radiation and graphite monochromator. The infrared absorption spectra (IR) were recorded on a Perkin Elmer Model 180 spectrophotometer with the samples dispersed in KBr discs. Simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) were carried out on ULVAC Thermal Analyzer in flowing stream of dry air and argon atmosphere at the rate of 10°C min^{-1}. All the experiments were carried out in platinum crucible with preheated alumina as reference material for DTA. The gases used were of high purity.

Analysis

The compounds were analyzed for their uranium, oxalate, carbon, hydrogen and water contents. Uranium was estimated potentiometrically using the Davies and Gray method [7] and oxalate by volumetric titration with $KMnO_4$. The carbon and hydrogen analysis were carried out on a Carlo Erba elemental analyzer. Water content was determined from the thermogravimetric curves. The results of the analysis are shown in Table 1. The analysis result confirmed the compounds to be $Rb_2UO_2(C_2O_4)_2 \cdot 2H_2O$ and $Cs_2UO_2(C_2O_4)_2 \cdot 2H_2O$.

Table 1 Chemical analysis in mass %

Compound	$Rb_2UO_2(C_2O_4)_2 \cdot 2H_2O$		$Cs_2UO_2(C_2O_4)_2 \cdot 2H_2O$	
	found	calcd	found	calcd
Uranium	36.11	36.45	31.18	31.31
Oxalate	26.95	27.10	24.30	23.62
Carbon	7.40	7.35	6.35	6.40
Hydrogen	0.60	0.61	0.53	0.53

Results and discussion

Thermal studies of $Rb_2UO_2(C_2O_4)_2 \cdot 2H_2O$

TG and DTA curves were recorded up to 1000°C. Figures 1 and 2 show the thermal decomposition of $Rb_2UO_2(C_2O_4)_2 \cdot 2H_2O$ in flowing atmosphere of dry air and argon

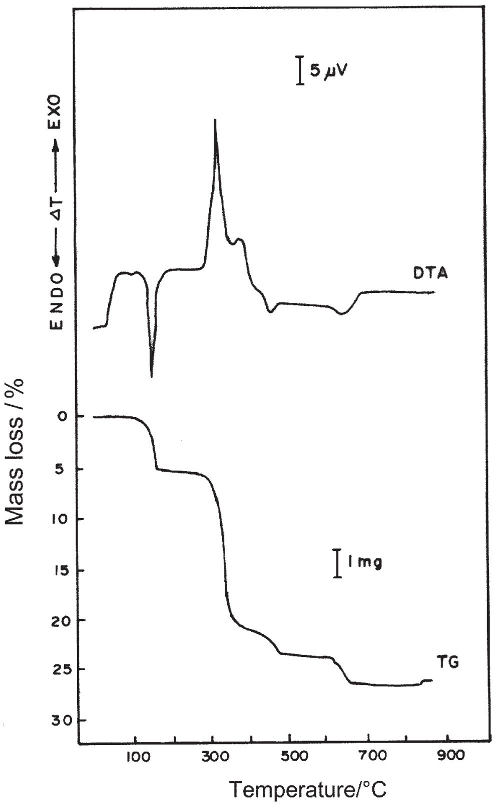

Fig. 1 TG and DTA curves of $Rb_2UO_2(C_2O_4)_2 \cdot 2H_2O$ recorded at 10°C min^{-1} in air. Mass of the sample 36.6 mg

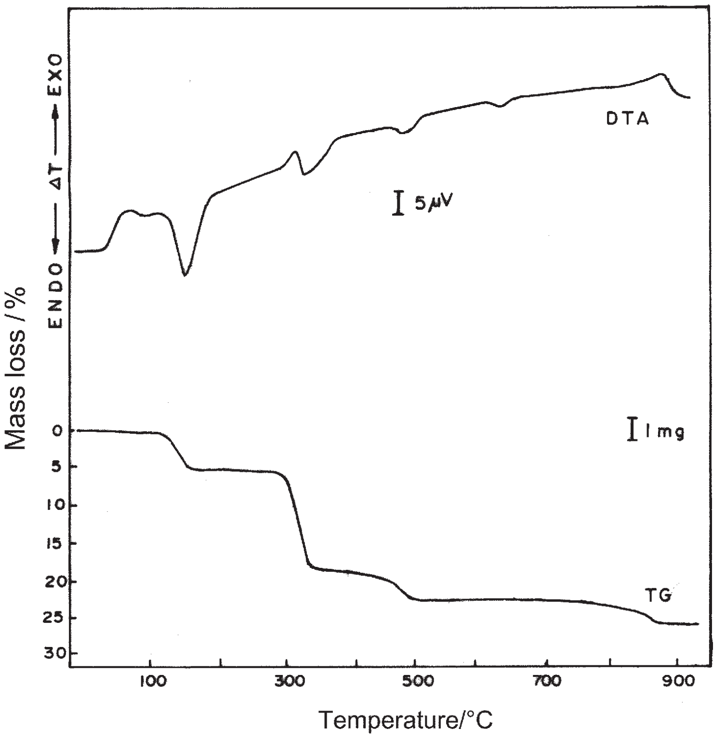

Fig. 2 TG and DTA curves of $Rb_2UO_2(C_2O_4)_2\cdot2H_2O$ recorded at 10°C min^{-1} in argon. Mass of the sample 35.83 mg

gas. Four steps are clearly seen in TG curves. The corresponding DTA also showed exothermic or endothermic DTA peaks indicating that the mass loss of compound occurred in four stages to form the monouranate. In both atmospheres two water molecules were lost in a single step, corresponding to endothermic DTA peaks centered around 160 and 155°C respectively. The analysis of the TG curves indicated that the water molecules were lost at 100 to 180°C. Isothermal heating at 180°C for few h gave the exact water loss of the compound. The loss in mass of the compound corresponds to the loss of the two water molecules both under argon and air. The X-ray diffraction pattern of anhydrous compound $Rb_2UO_2(C_2O_4)_2$ was found to be diffuse. Anhydrous rubidium uranyl oxalate was stable up to 300°C as indicated by TG curve. The second and third mass loss steps start after 300°C.

The thermal decomposition of anhydrous compound is highly exothermic and very fast in dry air atmosphere, while comparatively slow in argon atmosphere. This is due to oxidation of carbon monoxide to carbon dioxide in air. The reaction in air gave two exothermic DTA peaks at 330 and 395°C and one endothermic peak at 475°C. A definite plateau was observed after 475°C. From 475 to 620°C there was no mass loss. The fourth mass loss started after 620°C accompanied by an endothermic DTA peak at 630°C. In

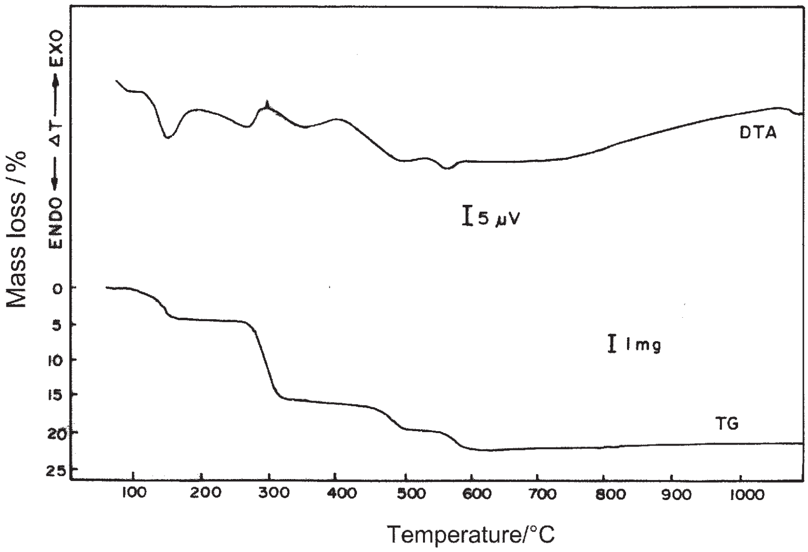

Fig. 3 TG and DTA curves of $Cs_2UO_2(C_2O_4)_2{\cdot}2H_2O$ recorded at 10°C min^{-1} in air. Mass of the sample 32.48 mg

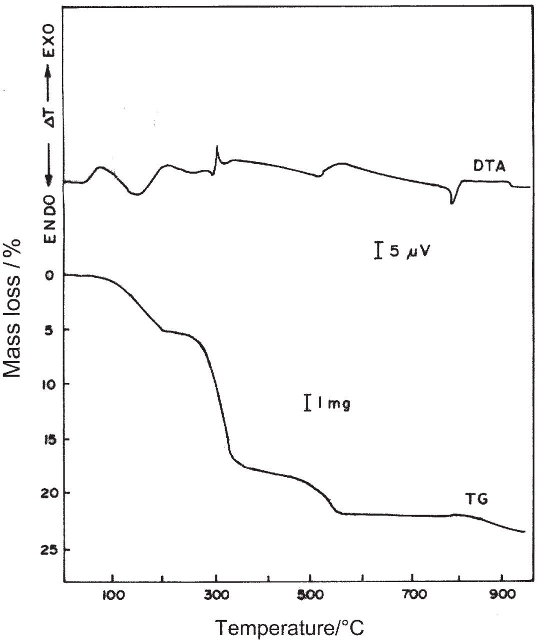

Fig. 4 TG and DTA curves of $Cs_2UO_2(C_2O_4)_2{\cdot}2H_2O$ recorded at 10°C min^{-1} in argon. Mass of the sample 74.75 mg

both atmospheres the final product of decomposition after heating upto 700°C was identified as Rb_2UO_4 and therefore, identical mass loss was observed.

In argon atmosphere the decomposition of anhydrous compound occurred below 400°C with endothermic peak at 330°C. The fourth mass loss occurred after 480°C. The mass loss at 600°C corresponded to the formation of $RbUO_3$. When the compound was heated up to 800°C the mass loss was not complete. XRD pattern of heated product showed that the XRD patterns matched that of $RbUO_3$. Isothermal heating at 800°C for 2 to 3 h gave Rb_2UO_4. The observed mass loss of 27.48% is in agreement with that calculated for conversion to Rb_2UO_4 (27.52%). In order to identify the intermediate products formed in the thermal decomposition the samples were heated in air and argon at 350°C for few h. The product obtained in argon gave UO_2 and Rb_2CO_3. The formation of UO_2 was confirmed by XRD pattern, while that of carbonate by the IR spectra. The mass loss was in agreement with the formation of Rb_2CO_3 and UO_2 as intermediates which reacted at 650°C to form Rb_2UO_4. Heating in air, however, did not show the presence of UO_2 probably because in air it reacted immediately with Rb_2CO_3. When the compound was heated up to 1000°C the product correspond to the formation of $Rb_2U_2O_7$.

Thermal studies of $Cs_2UO_2(C_2O_4)_2{\cdot}2H_2O$

TG and DTA curves were recorded up to 1000°C for $Cs_2UO_2(C_2O_4)_2{\cdot}2H_2O$. The thermal decomposition in flowing atmospheres of air and argon are shown in Figs 3 and 4 respectively. In both atmospheres the compound lost two water molecules below 150°C in a single step which was accompanied by endothermic DTA peaks at 145 and 150°C respectively. The anhydrous compound remained stable up to 280°C. The product obtained at 650°C was identified from its XRD pattern to be Cs_2UO_4. Although the nature of mass loss in both atmospheres were almost identical but the DTA curves were different. While the reaction between 280 and 450°C in air was accompanied by two exothermic peaks at 300 and 400°C and in argon had an endothermic peak at 310 and one exothermic peak at 330°C. Above 450°C there was a weak endothermic peak around 790°C.

In the absence of any clear plateau in the TG curve where DTA indicated a reaction, identification of the intermediate reaction products were tried by heating the sample at 350°C for long duration. The product obtained in argon at 350°C gave the XRD pattern of UO_2 whereas that in air diffuse pattern was obtained. The mass losses were in agreement with the formation of Cs_2CO_3 and UO_2. (Found 20.84%; calculated 20.33%.)

The formation of M_2UO_4 even under low oxygen potential conditions as in the case of Cs_2UO_4 [7] is a measure of the stability of this structure.

It is observed that when $Cs_2UO_2(C_2O_4)_2{\cdot}2H_2O$ was heated at 400 to 450°C for 10–15 h in furnace, the mass loss corresponds to the formation of Cs_2UO_4. This compound is very hygroscopic and therefore very difficult to record XRD pattern. Cs_2UO_4 decomposes at 650°C during which $Cs_2U_2O_7$ and $Cs_4U_5O_{17}$ are formed successively. The latter compound in turn decomposes very slowly into $Cs_2U_4O_{13}$ at 1000°C.

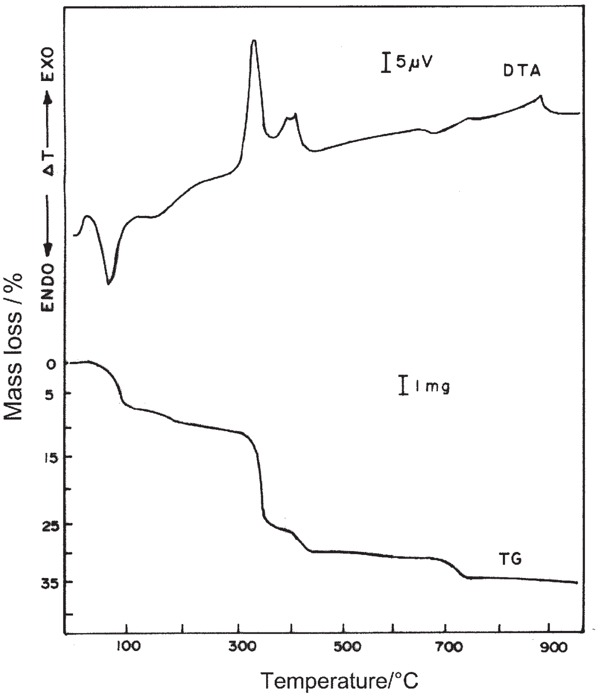

Fig. 5 TG and DTA curves of $K_2UO_2(C_2O_4)_2{\cdot}3H_2O$ recorded at 10°C min^{-1} in air. Mass of the sample 37.9 mg

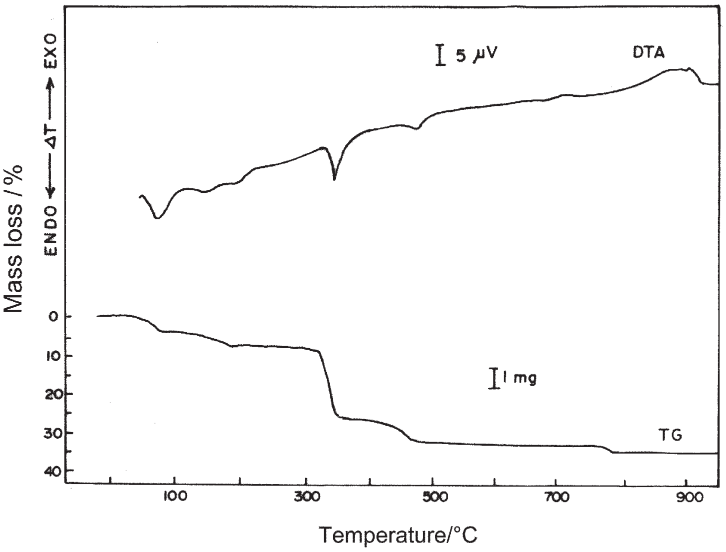

Fig. 6 TG and DTA curves of $K_2UO_2(C_2O_4)_2{\cdot}3H_2O$ recorded at 10°C min^{-1} in argon. Mass of the sample 25.7 mg

Thermal studies of $K_2UO_2(C_2O_4)_2\cdot 3H_2O$

TG and DTA curves were recorded up to 900°C. The thermal decomposition of $K_2UO_2(C_2O_4)_2\cdot 3H_2O$ in flowing atmosphere of dry air and argon gas are shown in Figs 5 and 6 respectively. In both atmospheres the compound lost three water molecules below 190°C in two steps accompanied by endothermic DTA peaks at 50 and 140°C. In dry air the anhydrous compound remained stable up to 290°C above which mass loss continued up to 750°C. The product obtained at 700°C was identified from its XRD pattern to be K_2UO_4. The reaction between 300 and 480°C in air was accompanied by two exothermic DTA peaks at 350 and 415°C with shoulder at 395°C. Above 450°C there was weak endothermic peak at 690°C corresponding to the formation of K_2UO_4.

In argon atmosphere the anhydrous compound remained stable up to 300°C above which mass loss continued up to 770°C. The reaction between 300 and 500°C in argon atmosphere was accompanied by two endothermic DTA peaks at 350 and 480°C. In argon atmosphere the reaction is comparatively slow and isothermal heating at 800°C for 2 to 3 h gave K_2UO_4. The observed mass loss of 34.98% is in agreement with that calculated for conversion to K_2UO_4 (34.24%).

It therefore follows that the thermal decomposition of potassium, rubidium and caesium uranyl oxalate can be represented as:

$$M_2UO_2(C_2O_4)_2\cdot nH_2O \xrightarrow[-nH_2O]{100\text{ to }160^\circ C} M_2UO_2(C_2O_4)_2 \xrightarrow{\sim 300^\circ C}$$

$$UO_2+M_2C_2O_4 \xrightarrow[-CO]{300\text{ to }400^\circ C} UO_2+M_2CO_3 \xrightarrow{700\text{ to }800^\circ C} M_2UO_4$$

$$CO+1/2O_2 \xrightarrow{\text{air}} CO_2\ (\text{exothermic})$$

(M=K, Rb and Cs)

The decomposition of oxalates is known to proceed with the evolution of CO gas which is endothermic reaction in inert atmosphere. In air, the oxidation of CO to CO_2 gives exothermic DTA peak during the thermal decomposition of the compounds.

X-ray and infrared spectroscopic studies

The X-ray diffraction patterns of $Rb_2UO_2(C_2O_4)_2\cdot 2H_2O$ and $Cs_2UO_2(C_2O_4)_2\cdot 2H_2O$ are shown in Tables 2 and 3 and could be indexed on orthorhombic unit cells. The cell parameters are also given in Tables 2 and 3. The density of the compounds were determined by pycnometric method using toluene. The measured and calculated densities are in good agreement and the number of formula units per cell is 4.

The infrared spectra of the two oxalates were similar. Both have absorption bands from the water molecules and coordinated oxalate groups as shown in Table 4. The infrared spectrum of $K_2UO_2(C_2O_4)_2\cdot 3H_2O$ has been discussed in terms of a simple penta co-ordinated arrangement involving two bidentate oxalate groups and a water molecule [5, 9]. As a result this compound loses water molecule in two steps. The similarity of the IR bands with those of the potassium salt suggest similarity in structure.

Table 2 X-ray diffraction pattern of $Rb_2UO_2(C_2O_4)_2 \cdot 2H_2O$, $\lambda=1.5418$ Å, $a=10.959(3)$ Å, $b=17.176(2)$ Å, $c=7.671(3)$ Å, $Z=4$. Density calcd=3.00 g cm^{-3}. Density obsd= 3.02 g cm^{-3}

d_{obsd}	d_{calcd}	h	k	l	I/I_o
6.76	6.76	1	2	0	10
5.90	5.90	1	1	1	80
5.22	5.22	2	1	0	20
4.46	4.46	2	0	1	50
4.30	4.30	0	4	0	10
3.96	3.96	2	3	0	45
3.75	3.75	0	4	1	20
3.50	3.50	0	2	2	40
3.36	3.36	3	2	0	100
3.28	3.28	1	5	0	70
3.24	3.24	3	1	1	70
3.19	3.19	0	3	2	10
2.86	2.86	0	6	0	15
2.767	2.767	1	4	2	10
2.68	2.68	0	6	1	20
2.58	2.58	4	0	1	40
2.50	2.50	3	5	0	10
2.38	2.38	3	5	1	15
2.353	2.352	4	3	1	30
2.296	2.296	2	1	3	10
2.244	2.245	1	6	2	20
2.200	2.197	0	4	3	25
2.157	2.158	4	2	2	80
2.109	2.108	1	8	0	10
2.062	2.063	4	5	1	10
1.933	1.934	2	7	2	25
1.922	1.921	2	5	3	25
1.747	1.748	1	7	3	20
1.741	1.740	5	6	0	20

Table 3 X-ray diffraction pattern of $Cs_2UO_2(C_2O_4)_2 \cdot 2H_2O$, λ=1.5418 Å, a=9.315(2) Å, b=15.999(1) Å, c=12.109(3) Å, Z=4. Density obsd=2.80 g cm^{-3}. Density calcd= 2.75 g cm^{-3}

d_{obsd}	d_{calcd}	h	k	l	I/I_o
6.07	6.07	1	2	0	90
5.07	5.08	1	0	2	5
4.47	4.47	2	1	0	10
4.19	4.19	2	1	1	45
4.03	4.03	2	2	0	100
3.61	3.61	1	1	3	15
3.36	3.36	1	2	3	10
3.22	3.22	0	3	3	30
3.02	3.02	1	5	0	60
2.61	2.61	0	6	1	25
2.51	2.51	2	1	4	15
2.42	2.42	1	5	3	30
2.29	2.29	4	0	1	15
2.15	2.15	1	3	5	30
2.08	2.08	1	7	2	30
2.01	2.01	2	6	3	60
1.72	1.72	3	4	5	50

Table 4 Infrared spectra of alkali metal uranyl oxalate hydrates (cm^{-1})

Assignment	K [9]	Rb	Cs
νOH		3630, 3390	3410, 3630
ν_{as}CO	1727, 1718, 1655	1715, 1685, 1655	1715, 1655
ν_{sy}CO	1455, 1420, 1288 1270	1450, 1405, 1380, 1295, 1250	1435, 1405, 1280, 1250
ν_{as}O–U–O	927	925	920
ν_{sy}O–U–O	840	835	830
O–C–O	787, 740	785	785

The thermal decomposition scheme discussed above is further confirmed by the IR spectra of these compounds heated to about 350°C in argon atmosphere. Spectral bands due to carbonate appear in the range 1100–1055 cm^{-1} and uranyl bands in the range 950–920 cm^{-1} disappear as expected. In argon atmosphere the reactions are comparatively slow and formation of UO_2 could be observed. When heated in air formation of intermediate compound UO_2 is not observed.

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The authors are thankful to Dr. D. D. Sood, Director, Radiochemistry and Isotope Group for his keen interest and constant encouragement during the course of this work.

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